

# Residence time statistics for $N$ blinking quantum dots and other stochastic processes

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We present a study of residence time statistics for  $N$  blinking quantum dots. With numerical simulations and exact calculations we show sharp transitions for a critical number of dots. In contrast to expectation the fluctuations in the limit of  $N \rightarrow \infty$  are non-trivial. Besides quantum dots our work describes residence time statistics in several other many particle systems for example  $N$  Brownian particles. Our work provides a natural framework to detect non-ergodic kinetics from measurements of many blinking chromophores, without the need to reach the single molecule limit.

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Residence time statistics has attracted considerable interest as a tool describing non-equilibrium phenomena. For a fluctuating time trace  $\mathcal{I}(t)$  the residence time  $t^+$  is the total time the signal remains beyond some threshold. A classical result in this field is Lévy's arcsine law [1, 2]. Then  $t^+$  is the residence time of a one dimensional Brownian particle in half space. In contrast with naive expectation the PDF of  $t^+/t$  ( $t$  is the measurement time) is not centered on its mean, instead it has a  $\cup$  shape with singularities described by the persistence exponent  $\alpha = 1/2$  for simple diffusion [3] (see details below). Similar bi-modal distributions were obtained for random walks in disordered environments [4], the persistence problem of diffusion in dimension  $d$  [5], a melting heteropolymer Sinai model [6] and for the fluorescence signal from a quantum dot (QD) [7, 8]. A *single* QD when interacting with a continuous wave laser field exhibits blinking with power law kinetics which is related to non trivial residence times, non-stationary and non ergodic behavior [7–10]. At random times the dot will switch from a bright state where many photons are emitted to a dark state (see Fig. 1). Probability density function (PDF) of on and off times are power laws  $\psi(\tau) \sim \tau^{-(1+\alpha)}$  at least for low laser intensity [11]. In most cases  $\alpha \simeq 1/2$  though  $1/2 < \alpha < 1$  was also reported. Most interestingly the average on and off times  $\langle \tau \rangle = \int_0^\infty \tau \psi(\tau) d\tau$  diverges, i.e. the dynamics is scale free. Several physical models explaining this behavior were suggested [9, 10], for example based on normal diffusion [8], however so far no experimental smoking gun provides confirmation to a specific mechanism responsible for the power law blinking. Further the effect is not limited to QDs, it is found also for organic single molecules provided that they are embedded in a disordered material [10]. One can rightly wonder why after many decades of spectroscopy we find surprises once individual objects are detected [12]. Can we not infer the strange blinking from measurements of many dots/single molecules? In particular can the broken ergodicity previously measured for an individual dot [7, 8] be detected also for an ensemble of dots?

For that aim we investigate the problem of residence time statistics for  $N$  blinking dots. We will soon show

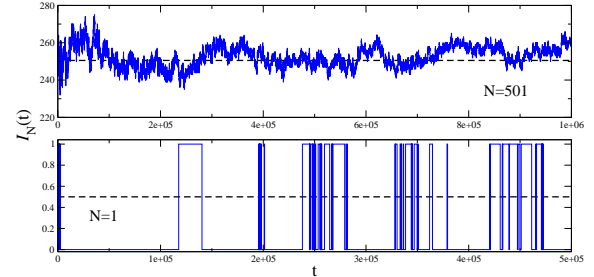


FIG. 1: Model two state blinking QD dot with  $\alpha = 1/2$ . For  $N = 1$  (lower panel) power law distributed sojourn times in bright +1 and dark 0 states lead to long residence times, of the order of the measurement time, in both states. Upper panel exhibits a superposition of the signal from  $N = 501$  processes. In this Letter we investigate the fluctuations of the residence time, namely the time the signal remains above the ensemble mean (the dashed line) showing they are not trivial even in the limit of  $N \rightarrow \infty$ .

that this problem can be mapped onto an interesting many particle Brownian problem and other stochastic processes. Surprisingly non trivial residence time statistics is found here even in the limit of  $N \rightarrow \infty$ . This is an important indication that by the analysis of light emitted from an ensemble of chromophores we may detect the strange kinetics without the need to reach the single molecule limit. We investigate transitions in the PDF of residence times (from  $\cup$  to  $\cap$  shape, as explained below) which are controlled by the number of dots  $N$ . We show that a critical number of dots marks a border line between the single particle domain and the many particle limit. Surprisingly we find values of  $\alpha$  below which  $\cup$  shape PDFs are robust, namely for certain  $\alpha$  the  $\cup$  shape PDF is found even for  $N \rightarrow \infty$ . Roughly speaking this is an important indication that elements of Lévy's arcsine law survive the  $N \rightarrow \infty$  limit, hence persistence exponents [3] from signals composed of a super-position of many elements are more common than expected. Our main analytical calculation is an exact expression for the variance of the residence time which is used to identify transitions between sub and super uniform statistics de-

finned below.

*Model and observable.* We consider  $N$  independent though statistically identical QDs. Each dot undergoes the following simple renewal process. The dot can be in a bright state where the intensity of light is  $I_i(t) = 1$  or a dark state with intensity  $I_i(t) = 0$ . Sojourn times in state on and off are independent identically distributed random variables with a common PDF  $\psi(\tau)$ .  $\psi(\tau)$  is moment less, namely for large  $\tau$   $\psi(\tau) \sim A\tau^{-(1+\alpha)}$  and  $0 < \alpha < 1$ . The signal of  $N$  dots is  $\mathcal{I}_N(t) = \sum_{i=1}^N I_i(t)$  whose ensemble mean is obviously  $\langle \mathcal{I}_N \rangle = N/2$ . Here we investigate the time  $t_+$  the process remains above its mean (see Fig. 1). The residence fraction is defined as  $0 < p^+ = t^+/t < 1$  where  $t$  is the total measurement time.

*Relation with Brownian motion.* The model and its variants describe many physical systems and processes beyond QDs e.g. well known Lévy walks [13] which describe tracer diffusion in turbulent flow, certain chaotic systems [14] and recently models of  $1/f$  noise [15, 16]. Probably the best well known example is Brownian motion. Consider a single Brownian particle in one dimension and let  $I_1(t) = 1$  for a particle being in  $x > 0$  and  $I_1(t) = 0$  for  $x < 0$ . As well known the PDF of first passage times and hence of sojourn times in  $x < 0$  or  $x > 0$  follow power law behavior  $\psi(\tau) \propto \tau^{-3/2}$  and hence  $\alpha = 1/2$ . For a single particle the time  $t^+$  is simply the residence time in half space  $x > 0$  which follows the classical arcsine distribution of P. Lévy (see details below). For  $N$  Brownian particles  $t^+$  is the time the majority of  $N$  particles are on  $x > 0$ . Naively one would expect that this time in the  $N \rightarrow \infty$  limit would be equal to half of the measurement time. This turns out to be wrong and features of Lévy's arcsine law survive the  $N \rightarrow \infty$  limit.

*Known results for a single QD  $N = 1$ .* Lamperti obtained the PDF of the residence fraction  $0 < p^+ < 1$  [1, 8]

$$l_a(p^+) = \frac{[\sin(\pi\alpha)/\pi] (p^+)^{\alpha-1} (1-p^+)^{\alpha-1}}{(p^+)^{2\alpha} + 2(p^+)^{\alpha} (1-p^+)^{\alpha} \cos(\pi\alpha) + (1-p^+)^{2\alpha}}. \quad (1)$$

When  $\alpha = 1/2$  the mentioned arcsine PDF is obtained which has a  $\cup$  shape. When  $\alpha \rightarrow 1$  the PDF Eq. (1) approaches a delta function on its mean  $\langle p^+ \rangle = 1/2$  which corresponds to ergodic behavior. In the opposite limit  $\alpha \rightarrow 0$  we have two delta functions on  $p^+ = 0$  and  $p^+ = 1$ . Then the QD is either in the dark state or the bright state for the whole duration of the measurement. An important feature of the Lamperti PDF is that for  $0 < \alpha < 1$  the maximum of the PDF is on these rare event: the PDF diverges on  $p^+ = 0$  and  $p^+ = 1$ . This clearly reflects sojourn times in either the on or the off state which are of the order of the measurement time.

*The PDF of the residence fraction* was obtained numerically and is presented in Fig. 2 for  $\alpha = 0.57$  and  $\alpha = 0.5$ . For  $\alpha = 0.57$  a transition from a  $\cup$  shape PDF for  $N < 5$

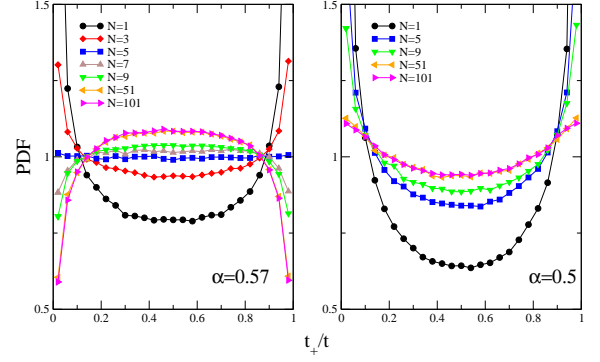


FIG. 2: Left panel  $\alpha = 0.57$  the PDF of residence fraction exhibits a transition between a  $\cup$  to  $\cap$  shape PDF which is controlled by  $N$ . In contrast such a transition is not observed for  $\alpha = 0.5$  and for smaller values of  $\alpha$  (not shown).

to a  $\cap$  shape PDF for  $N > 5$  is found, while  $N = 5$  gives a uniform PDF. In contrast, for  $\alpha = 0.5$  the PDF for all  $N$  has a  $\cup$  shape. These findings indicate: (i) even in the large  $N$  limit the fluctuations of residence times remain non-trivial, namely we do not see a convergence of the PDF to a delta function and (ii) that there exists a critical  $\alpha$  below which the PDF of residence fractions has always (for any  $N$ ) a  $\cup$  shape. However, simulations are limited to finite  $N$  and finite measurement time, hence we now turn to analytical theory.

*The residence fraction for  $N$  QDs is*

$$p^+ = \frac{1}{t} \int_0^t \theta[\mathcal{I}_N(t') - N/2] dt' \quad (2)$$

where  $\theta(x)$  is the step function:  $\theta(x) = 1$  if its argument is positive, otherwise it is zero. For convenience we will consider only odd  $N$ . The states of the system are determined by a vector  $[I_1(t), \dots, I_i(t), \dots, I_N(t)]$ . States contributing to the considered residence fraction are those with at least  $(N+1)/2$  processes in bright state  $I_i(t) = 1$  and we have  $2^N/2$  such states. We can rewrite the residence fraction as a sum over time averages of these states

$$p^+ = \frac{1}{t} \int_0^t \sum_{j=0}^{N-1} \Pi_{i=1}^N I_i(t') \bullet^j dt'. \quad (3)$$

Here  $\Pi_{i=1}^N I_i \bullet^j$  is a sum over all permutation of the product  $I_1 \dots I_N$  with  $j$  terms of the type  $1 - I_i$  and  $N - j$  terms of the type  $I_i$ . For example for  $N = 3$  we have  $\Pi_{i=1}^3 I_i \bullet^0 = I_1 I_2 I_3$  for  $j = 0$  and  $\Pi_{i=1}^3 I_i \bullet^1 = (1 - I_1) I_2 I_3 + I_1 (1 - I_2) I_3 + I_1 I_2 (1 - I_3)$ . This means that  $p^+$  has contributions from states  $(1, 1, 1)$  (all dots bright) or  $(0, 1, 1)$ ,  $(1, 0, 1)$ ,  $(1, 1, 0)$  since for these states the total intensity  $\mathcal{I}_{N=3}(t)$  is above its mean  $\langle \mathcal{I} \rangle_{N=3} = 3/2$ .

*Sub and super uniform statistics.* It is easy to see that the mean is  $\langle p^+ \rangle = 1/2$  which is expected from symmetry. More interesting is the variance  $\sigma^2 = \langle (p^+)^2 \rangle - \langle p^+ \rangle^2$ .

$N$	$\sigma^2$
5	$36C_5 - 45C_4 + 25C_3 - \frac{15}{2}C_2 + \frac{15}{8}C_1 - \frac{1}{4}$
7	$400C_7 - 700C_6 + 546C_5 - 245C_4 + 70C_3 - \frac{105}{8}C_2 + \frac{35}{16}C_1 - \frac{1}{4}$
9	$4900C_9 - 11025C_8 + 11250C_7 - 6825C_6 + \frac{10899}{4}C_5 - \frac{5985}{8}C_4 + \frac{1155}{8}C_3 - \frac{315}{16}C_2 + \frac{315}{128}C_1 - \frac{1}{4}$

TABLE I: Variance of the residence fraction  $\sigma^2$  for various  $N$ .

The variance can be used to quantify different types of fluctuations. If  $\sigma^2 > 1/12$  we define the fluctuations as super-uniform while  $\sigma^2 < 1/12$  is sub-uniform. Distributions of residence fractions with  $\cup$  ( $\cap$ ) shape are super-uniform (sub-uniform) respectively. Squaring Eq. (3) and averaging with respect to the random process

$$\langle (p^+)^2 \rangle =$$

$$\frac{1}{t^2} \sum_{l=0}^{N-1} A_N(l) \int_0^t dt_1 \int_0^t dt_2 \langle I(t_1) [1 - I(t_2)]^l \rangle \langle I(t_1) I(t_2) \rangle^{N-l} \quad (4)$$

We see that the fluctuation of the residence fraction is determined by the intensity correlation function  $\langle I(t_1) I(t_2) \rangle$  (here  $\langle I(t_1) [1 - I(t_2)] \rangle = 1/2 - \langle I(t_1) I(t_2) \rangle$ ). A lengthy combinatorial calculation, which we will publish elsewhere, yields the coefficients  $A_N(l)$

$$A_N(l) = \begin{cases} \binom{N}{l} 2^{N-1} [1 - S_N(l)] & \text{if } l \leq \frac{N-1}{2} \\ \binom{N}{l} 2^{N-1} S_N(N-l) & \text{if } l \geq \frac{N-1}{2}, \end{cases} \quad (5)$$

where [17]

$$S_N(l) = 2 \sum_{i=0}^{\lfloor \frac{l-1}{2} \rfloor} \binom{l}{i} \frac{1}{2^i} \frac{1}{2^{l-i}} \sum_{\tilde{i}=\frac{N+1}{2}-l+i}^{\frac{N-1}{2}-i} \binom{N-l}{\tilde{i}} \frac{1}{2^{N-l-\tilde{i}}} \frac{1}{2^{\tilde{i}}}. \quad (6)$$

This representation will soon be useful since we identify binomial expansions in it.

*Correlation functions.* Many natural processes exhibit stationary behavior namely  $\langle I(t_1) I(t_2) \rangle$  is a function of the time difference  $|t_2 - t_1|$ . However many other systems exhibit aging

$$\langle I(t_1) I(t_2) \rangle = \mathcal{C}(t_1/t_2) \quad t_1/t_2 < 1, \quad (7)$$

which is common for a system with infinite mean waiting time. For the two state QD process [1, 8]

$$\mathcal{C}(z) = \frac{1}{4} \left[ \frac{\sin \pi \alpha}{\pi} B(z; \alpha, 1 - \alpha) + 1 \right] \quad 0 < z < 1 \quad (8)$$

and  $B(z; \alpha, 1 - \alpha) = \int_0^z x^{\alpha-1} (1-x)^{-\alpha} dx$  is the tabulated incomplete Beta function.

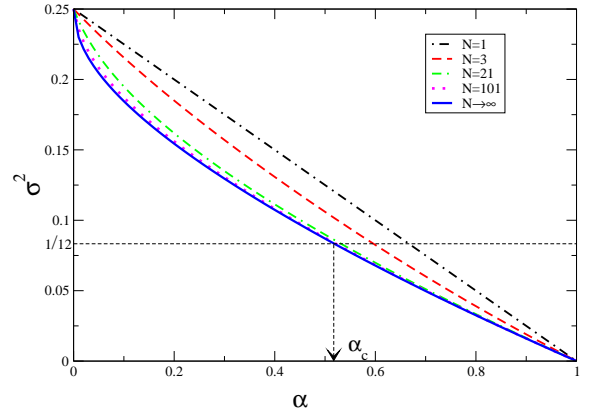


FIG. 3: The variance of the residence fraction versus  $\alpha$  for various number of processes  $N$ . When  $\alpha \rightarrow 1$  the process turns ergodic and the variance is zero. For  $\alpha < 1$  even when  $N \rightarrow \infty$  the fluctuations remain finite, indicating that in principle the non-ergodic kinetics so far detected on the single particle level can be found already for a large ensemble of particles. Even more surprisingly, for  $N \rightarrow \infty$  the fluctuations remain super-uniform, i.e. the variance is larger than  $1/12$ , when  $\alpha < \alpha_c = 0.518\dots$ . This implies that a  $\cap$  shape PDF of the residence times does not describe fluctuations when  $\alpha < \alpha_c$ .

*Fluctuations for finite  $N$ .* Inserting Eq. (8) in Eq. (4) changing variables to  $z = t_1/t_2$  we find exact expressions for the fluctuations. For  $N = 1$   $\sigma^2 = 1 - \alpha$ , while for  $N = 3$

$$\sigma^2 = 4C_3 - 3C_2 + \frac{3}{2}C_1 - \frac{1}{4} \quad (9)$$

where

$$C_n = \int_0^1 C^n(z) dz. \quad (10)$$

Cases  $N = 5, 7, 9$  are reported in Table 1 and similarly we obtain  $\sigma^2$  for any finite  $N$  using the exact expression for  $A_N(l)$ . With Table 1 we can determine whether fluctuations are sub or super uniform. For example for  $N = 5$  we find uniform statistics  $\sigma^2 = 1/12$  when  $\alpha \simeq 0.57$ . This perfectly matches the simulations in Fig. 2 which exhibit a uniform distribution of the occupation fraction for these parameters. For  $\alpha = 1/2$ , i.e. Brownian motion, Eqs. (8,10) give

$$C_n = \sum_{m=0}^n \binom{n}{m} \frac{(i\pi)^{-m}}{4^{n+1}} [m! - \Gamma(1+m, -i\pi) - \Gamma(1+m, i\pi)]. \quad (11)$$

For  $\alpha \neq 1/2$  we solve the integral Eq. (10) with Mathematica [18] and with Table 1 obtain numerically exact expressions for  $\sigma^2$ . In Fig. 3 we show  $\sigma^2$  versus  $\alpha$  for various  $N$ . When  $\alpha = 1$  we have  $C_n = \langle I \rangle^{2n} = 4^{-n}$  and then using Table 1 we get  $\sigma^2 = 0$  which corresponds to the ergodic phase. In the opposite limit  $\alpha \rightarrow 0$  we

have  $C_n = \langle I \rangle^n = 2^{-n}$  and then  $\sigma^2 = 1/4$ . This is the expected behavior since when  $\alpha \rightarrow 0$  a single particle remains in one state (either bright or dark) for the whole measurement time and hence with probability  $1/2$  the signal composed of an ensemble of an odd number of particles is above its mean all along the measurement. As shown in Fig. 3 the fluctuations are the strongest when  $N = 1$  which is expected. Surprisingly, we see that as the number of particles is increased the fluctuations remain finite. This means that the non ergodic behavior found for a single QD [7, 8] can be detected also for a large ensemble of dots. A measurement of the residence time  $t^+$  remains a random variable even when  $N$  is large and a single measurement is not a reproducible result. We now turn to find the variance  $\sigma^2$  in the  $N \rightarrow \infty$  limit.

*Limit  $N \rightarrow \infty$ .* The limit of large  $N$  and  $l$  is taken in such a way that  $x = l/N$  remain finite. We then use Stirling's formula to approximate the double binomial sum in Eq. (6) with a double integral over a pair of Gaussians. The first integration yields an error function and we find

$$S_N(l) \sim 2 \int_0^\infty \sqrt{\frac{xN}{2\pi}} e^{-\frac{N x^2}{2}} \text{Erf} \left( \frac{\sqrt{N} x z}{\sqrt{2\sqrt{1-x}}} \right) dz. \quad (12)$$

From a table of integrals  $S_N(l) \sim \frac{2}{\pi} \text{ArcSin}(\sqrt{x})$  and hence we find

$$A_N(l) \sim \binom{N}{l} 2^{N-1} \left[ 1 - \frac{2}{\pi} \text{ArcSin} \left( \sqrt{\frac{l}{N}} \right) \right]. \quad (13)$$

Inserting this expression in Eq. (4) and using Eq. (7) we find (after change of variables to  $z = t_1/t_2$ )

$$\langle (p^+)^2 \rangle \sim \int_0^1 dz \sum_{l=0}^N \frac{1}{2} \left[ 1 - \frac{2}{\pi} \text{ArcSin} \sqrt{\frac{l}{N}} \right] \binom{N}{l} [1 - 2\mathcal{C}(z)]^l [2\mathcal{C}(z)]^{N-l}. \quad (14)$$

In the large  $N$  limit the binomial part of the integral:  $\binom{N}{l} [1 - 2\mathcal{C}(z)]^l [2\mathcal{C}(z)]^{N-l}$ , is narrowly centered around its mean  $[1 - 2\mathcal{C}(z)] N$ . Hence we find

$$\lim_{N \rightarrow \infty} \sigma^2 = \frac{1}{\pi} \int_0^1 dz \text{ArcSin} \sqrt{2\mathcal{C}(z)} - \frac{1}{4}, \quad (15)$$

which is the main equation of this manuscript.

Eq. (15) shows that even when  $N \rightarrow \infty$  the statistics of blinking QDs is non ergodic: the fluctuation of the residence time are finite even for a large ensemble. Only in the limit  $\alpha \rightarrow 1$  we do get expected ergodic behavior  $\sigma^2 = 0$ . In Fig. 3 we plot Eq. (15) versus  $\alpha$  and classify sub-uniform and super-uniform statistics. For the Brownian case  $\alpha = 1/2$  we get  $\lim_{N \rightarrow \infty} \sigma^2 = 0.086 \dots$  which is super-uniform, hence this rigorously shows that a  $\cap$  shape PDF is not found [19]. Lévy's arcsine law exhibits

super-uniform statistics and surprisingly this property is maintained also for a large ensemble of particles. Inserting Eq. (8) in Eq. (15) we find that if  $\alpha < \alpha_c = 0.518 \dots$  the fluctuations are super-uniform in the limit  $N \rightarrow \infty$  (see Fig. 3). This theoretical prediction is in agreement our simulations presented in Fig. 2 which shows super-uniform (sub-uniform) behaviors when  $\alpha < \alpha_c$  ( $\alpha > \alpha_c$ ) respectively.

Bouchaud [20], introduced the profound concept of weak ergodicity breaking in the context of glassy dynamics. It holds for systems with power law sojourn times and with a phase space not broken into mutually inaccessible regions, e.g. blinking QDs. For a macroscopic system like a glass Bouchaud assumed that measurements are made on a large number of sub-systems (micro spin-glasses of clusters of magnetic atoms in his case) and that such measurements are disorder averaged. He claimed that performing dynamical experiments on *mesoscopic samples, where  $N$  is small*, would yield irreproducible results. Indeed we thoroughly believed this scenario at the start of this project, namely our naive expectation was that as the number of QDs increases we will approach an ergodic behavior. However, it turns out that a measurement of the residence time of  $N \rightarrow \infty$  QDs is irreproducible. Weak ergodicity breaking can be detected for a large ensemble of sub-systems.

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  - [17] Here  $\sum_A^B \dots = 0$  if  $B < A$ .
  - [18] Properties of  $C_n$  will be investigated elsewhere, e.g. for large  $n$  steepest descent gives  $C_n \sim$
- $$\Gamma\left(\frac{2-\alpha}{1-\alpha}\right) \left[\frac{\sin \pi \alpha}{(1-\alpha)2\pi}\right]^{-\frac{1}{1-\alpha}} \left(\frac{1}{2}\right)^n n^{-\frac{1}{1-\alpha}}.$$
- [19] Our exact expression for  $\sigma^2$  cannot be used to determine the existence of singularities in the PDF of  $t^+/t$ . From simulations we find that  $\alpha \simeq 1/2$  is a critical point in the sense that these singularities vanish in the  $N \rightarrow \infty$  limit.
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